as the 4′,5′- or 5′,6′-vinyl ether or which may open further to the hydroxy ketone **9** to allow exchange in a more conventional fashion.[14]

It was anticipated from experiments described in the accompanying paper[1] that in a dichlorovos-inhibited culture of *A. parasiticus*, multiply labeled averufin **7** would suffer conversion to versiconal acetate **10** having both ^{13}C and ^{2}H isotopes at C-1′, the hemiacetal carbon. For the sake of the envisioned experiment, a *deuterium* NMR spectrum[15] of this multiply labeled product was expected to provide the following: First, the 1′-D, which had been introduced in synthetic averufin[1] at a known level of enrichment (ca. 85%), would serve as an internal reference for integration of the other labeled centers. Second, if an intramolecular Baeyer–Villiger oxidation were operative, the integrated intensities of deuterium label at C-1′:4′:6′ ought to be 0.85:2:3. Whereas, if the terminal *O*-acetyl unit were derived trivially by intermolecular reaction with endogenous acetylCoA, an acetyl methyl signal of very low if detectable relative intensity would be expected at a clearly distinguishable chemical shift.

Averufin (**7**, 63 mg) was apportioned equally among 21 250-mL Erlenmeyer flasks containing 10 g of wet 48 h-old mycelial pellets of *A. parasiticus* (ATCC 15517) in 100 mL of a replacement medium[9a] and 10 ppm of dichlorovos and incubated for 40 h. In the $^{2}H\{^{1}H\}$ spectrum of the isolated versiconal acetate (Figure 1) the hemiacetal carbon 1′-D appears as a very broad resonance between δ 5.5 and 7. The breadth of this signal arises from several effects: low rotational mobility, ^{13}C coupling, and the fact that versiconal acetate in Me_2SO exists as an equilibrating mixture[7,8] of the hemiacetal shown in **10** and that formed to the anthraquinone 1-OH as well as a small amount of open form. A two-deuterium signal for C-4′ appears at δ 4.1, sharper owing to greater local molecular motion. Last, at about δ 1.9 a three-deuterium singlet is observed (with small acetone impurity to lower field), corresponding to retention of the trideuteriomethyl.

It may be concluded that in the formation of versiconal acetate (**5**) from averufin (**2**), an intramolecular Baeyer–Villiger-like oxidation[17] takes place to lead to the ultimate loss of the two terminal carbons of the averufin side chain as acetate in the course of bisfuran formation. Whether this oxidative cleavage occurs before or after the chain branching process where the anthraquinone nucleus migrates from C-1′ to C-2′ cannot be determined at present. However, given the constraint of deuterium retention at C-1′ from **2** to **5** and to C-13 in **1**, both the nature and sequence of the biosynthetic events may be explored in biochemical and stereochemical experiments with potential intermediates accessible by extension of the synthetic methods developed for this program.[18]

Acknowledgment. Professor J. W. Bennett (Tulane) is warmly thanked for assistance with microbiological aspects of this work. The National Institutes of Health are gratefully acknowledged for financial support (Grant ES 01670) and for providing partial funding to acquire the Bruker WM-300 instrument used (Grant GM 27512). We are pleased to note the essential services of NSF-supported instrument facilities at Yale University (Northeast Regional NMR Facility; 500 MHz) and The Johns Hopkins University (Middle Atlantic Mass Spectrometry Laboratory).

Registry No. (±)-**2**, 79896-28-9; (±)-[1-^{2}H,^{13}C]-**2**, 83152-86-7; **5**, 62886-00-4; (±)-**7**, 83199-79-5.

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[14] Monitoring exchange by ^{1}H NMR at 300 MHz revealed complete loss of proton intensity at C-4′ and C-6′. Similarly, mass spectral analysis gave a strong M + 7 for the major molecular species. Interestingly, exchange at the aryl positions is minimal within the limits of detection by ^{1}H or ^{2}H NMR.

[15] Garson, M. J.; Staunton, J. *J. Chem. Soc., Chem. Soc. Rev.* **1980**, *9*, 539–561.

[16] Hsieh, D. P. H.; Mateles, R. I. *Appl. Microbiol.* **1971**, *22*, 79–83.

[17] It is noted that such an oxidation may occur to carry the B-series aflatoxins to the G series. Mass spectral analysis of the latter was carried out to complete the proof that the side chain oxidative rearrangement of **7** to **10** is strictly intramolecular. An in-beam electron impact spectrum was obtained at 210 °C that failed to give a good molecular ion, but strong fragments[8] were observed for unlabeled versiconal acetate at *m/z* 382 ($M^+ - H_2O$) and 340 (M^+ – HOAc). Prominant peaks for the analogous fragments of **10** were seen at *m/z* 389 and 344, from whose relative intensities minimal specific incorporations of **7** were correspondingly computed to be 21% and 20%, respectively.

[18] Townsend, C. A.; Davis, S. G.; Christensen, S. B.; Link, J. C.; Lewis, C. P. *J. Am. Chem. Soc.* **1981**, *103*, 6885–6888. Townsend, C. A.; Bloom, L. M. *Tetrahedron Lett.* **1981**, 3923–3924.

Complexes of the New Ligand Tetracyanobiimidazole

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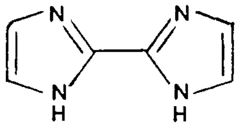
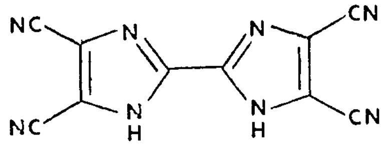
The search for planar, conjugated molecules, capable of forming stacked complexes, led to our previous investigations of 2,2′-biimidazole (H_2biim), **1**, which revealed a variety of structural possibilities.[1-3] Recently, in an effort to increase the polarizability and acceptor properties of our compounds, we have synthesized a remarkable new species, 4,4′,5,5′-tetracyano-2,2′biimidazole (H_2Tcbiim), **2**.



1



2

Whereas H_2Biim has been known for many years[4] and is readily synthesized from the bisulfite addition salt of glyoxal reacting with ammonia,[5] similar methods using diaminomaleonitrile (DAMN) and a variety of coupling reagents failed to produce H_2Tcbiim.[6] The preparation of H_2Tcbiim proceeds by a ring coupling reaction of 4,5-dicyanoimidazole with 2-diazo-4,5-dicyanoimidazole.[7] These reagents were prepared by the methods of the du Pont group.[8,9]

H_2Tcbiim is a colorless, high-melting, air-stable solid. It is somewhat more soluble in most solvents than H_2Biim and is far more acidic, $pK_1 \approx 2.1$, $pK_2 \approx 5.5$ measured in 40% (v/v) acetonitrile–0.1 M TEAP. The mass spectrum shows, in addition to a large parent ion peak at *m/e* 234.1, principally decomposition by loss of HCN and $(CN)_2$. Three ^{13}C NMR peaks appear at 140.8, 118.0, and 110.3 ppm relative to Me_4Si. Extended Hückel

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[1] Kaiser, S. W.; Saillant, R. B.; Rasmussen, P. G. *J. Am. Chem. Soc.* **1975**, *97*, 425.

[2] Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2681.

[3] Reference 2, p 2688.

[4] Debus, *Ann. Chem. Pharm.* **1859**, *107*, 199.

[5] Holmes, F.; Jones, K. M.; Torrible, E. G. *J. Chem. Soc.* **1961**, 4790.

[6] Hough, R. L., private communication.

[7] In a typical reaction, 0.01 mmol of 2-diazo-4,5-dicyanomidazole is prepared and added moist to 0.01 mmol of 4,5-dicyanoimidazole suspended in 30 mL of CCl_4. The slow evolution of nitrogen provides a convenient monitoring of the coupling reaction, which proceeds smoothly at 45 °C. **Caution**: The zwitterion 2-diazo-4,5-dicyanoimidazole decomposes explosively at 150 °C, as one might expect, given its unusual stoichiometry (C_5N_6).

[8] Sheppard, W. A.; Webster, O. W. *J. Am. Chem. Soc.* **1973**, *95*, 2695.

[9] D. W. Woodward, U.S. Patent 2534331, 1950.

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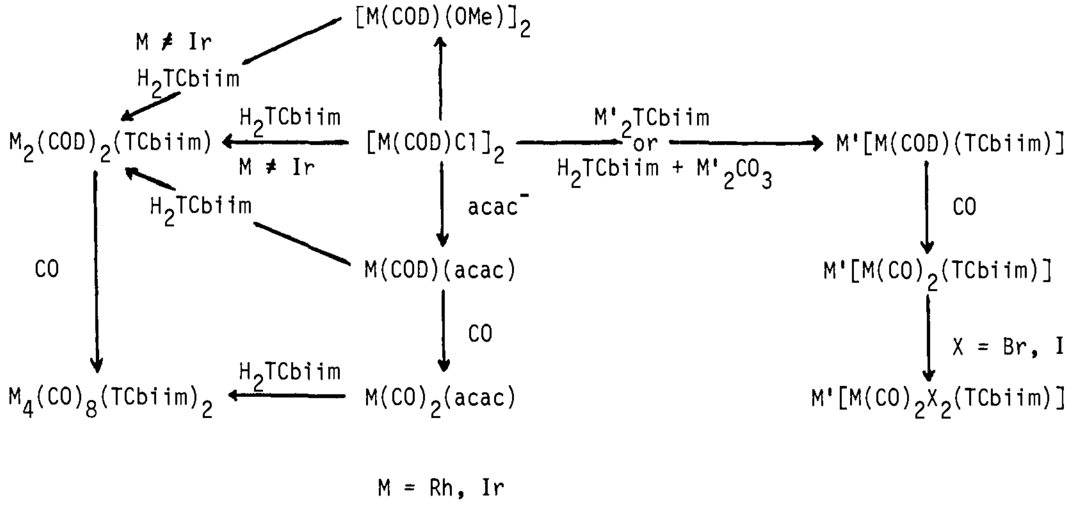
Scheme I



calculations[10] on the Tcbiim^{2-} give charge distributions in accord with the expectation of strong electron withdrawal by the nitriles through the π system. Cyclic voltammetry on bis(tetraethylammonium)Tcbiim in acetonitrile shows two reversible one-electron oxidation waves at 0.94 and 1.32 V vs. NHE, confirming the stability of the π-electron system of the anion.

As expected from its acidity, complexes of H_2Tcbiim are invariably in the dianionic form. Starting from aqueous $K_2M(CN)_4$, M = Ni, Pd, Pt, treatment with H_2Tcbiim gives white $K_2[M(CN)_2(Tcbiim)]$ although in the case of platinum the yield is low.[11] Susceptibility measurements on the nickel compound confirmed its diamagnetism, indicative of square-planar geometry.

The structure of these complexes is also apparent from the infrared spectra, which show absorptions typical of cis ionic cyanides with splittings of 5–20 cm^{-1} (~2140 cm^{-1}) and barely resolvable splitting of ≤7 cm^{-1} due to the inequivalent Tcbiim nitriles (~2225 cm^{-1}).

Preliminary analysis of these results suggested that Tcbiim^{2-} is a ligand of very low σ-donor strength and a strong π acceptor. These tendencies have been verified by the preparation of a series of complexes of Rh(I) and Ir(I). One useful starting material for synthesis of these complexes is M(COD)(AcAc)[12] (COD = 1,5 cyclooctadiene, AcAc = acetylacetone anion, M = Rh, Ir). Treatment of this material with 0.5 equiv of H_2Tcbiim affords dimers, similar to those formed by H_2biim but with greater tendency to solvate.

The COD is readily displaced in these compounds by CO, yielding tetramers of formula $M_4(CO)_8(Tcbiim)_2$, which again appear to mimic the complicated structures found for the H_2biim.[1-3] The reactions and interconversions that we have observed are summarized in Scheme I. The series of composition $M'[Ir(CO)_2(Tcbiim)]$, M' = K$^+$, Na$^+$, Li$^+$, N(Et)$_4^+$, are all yellow in dilute solution but show a variety of colors in the solid state, ranging from red with N(Et$_4$)$^+$ to dark blue with Li$^+$. These color changes suggested intermolecular interactions of the sort necessary for developing highly anisotropic properties. Accordingly we have attempted a number of oxidation experiments on these salts. Cyclic voltammetry in acetonitrile on $N(Et)_4[Ir(CO)_2(Tcbiim)]$ gives a reversible two-electron oxidation wave at 0.84 V. Bulk electrochemical oxidation of this salt yields a solid whose structure is still under investigation but that does not resemble the highly conducting anistropic materials. Oxidation by bromine or iodine yields several isomers of the expected oxidative addition products. These products do not react with the univalent iridium precursors to produce intermediate valence states.

The IR bands due to CO are typically shifted 5–25 cm^{-1} higher in H_2Tcbiim compounds compared to those of H_2biim compounds. Clearly, H_2Tcbiim is a ligand of strong π-accepting properties. Its synthetic versatility will allow the formation of a wide variety of compounds especially in combination with metals in low oxidation states. Although H_2Tcbiim has not thus far led us to highly conducting species, structural and synthetic studies are continuing.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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[10] Calculations were carried out by using the ICON 8 program with weighted H_{ij} formula. Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

[11] We used initially the prolonged reflux method of Kiernan and Ludi (Kiernan, P.; Ludi, A. *J. Chem. Soc., Dalton Trans.* **1978**, 1127). An improved but somewhat more elaborate procedure will be published elsewhere.

[12] Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1965**, 4997.

Facile Preparation of 2,3-Benzo-1,4-diphenyl-7-silanorbornadiene Derivatives and the First Clear Evidence of Silylene to Disilene Thermal Rearrangement[1]

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This paper describes the synthesis of the so far elusive[2,3] 2,3-benzo-1,4-diphenyl-7-silanorbornadiene derivatives (**1**), which undergo thermal extrusion of variously substituted silylenes. The first definitive evidence for the silylene–disilene rearrangement is also reported.

To a dichloromethane (40 mL) solution of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**3a**, 525 mg, 2.0 mmol; eq 1) and 1-aminobenzotriazole (**4**) (402 mg, 3.0 mmol) was added a dichloromethane (15 mL) solution of lead tetraacetate (90%, 1.48 g, 3.0 mmol) dropwise during 10 min at 0 °C. The mixture was subjected to flash chromatography through a short column (3 cm × 5 cm) packed with silica gel. Benzene was used as an eluent. Removal of the solvent gave a yellow viscous oil, from which 257 mg (38%) of colorless crystalline 2,3-benzo-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (**1a**, mp 108–109 °C) was obtained by addition of hexane followed by standing overnight in a re-

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[1] Chemistry of Organosilicon Compounds, 164.

[2] Gilman, H.; Cottis, S. G.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 1596. These authors have prepared stable 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**2**).

[3] **1** was presumed as a useful silylene generator but was recorded as thermally extremely unstable. See inter alia: (a) Maruca, R. *J. Org. Chem.* **1971**, *36*, 1626. (b) Barton, T. J.; Nelson, A. J.; Clardy, J. *Ibid.* **1972**, *37*, 895. (c) Maruca, R.; Fischer, R.; Roseman, L.; Gehring, A. *J. Organomet. Chem.* **1973**, *49*, 139. (d) Mayer, B.; Neumann, W. P. *Tetrahedron Lett.* **1980**, *21*, 4887. (e) Barton, T. J.; Goure, W. F.; Witiak, J. L.; Wulff, W. D. *J. Organomet. Chem.* **1982**, *225*, 87.

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